



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁶:

G01N 23/223

A1

(11) International Publication Number:

WO 00/16078

(43) International Publication Date:

23 March 2000 (23.03.00)

(21) International Application Number: PCT/US99/20867

(22) International Filing Date: 16 September 1999 (16.09.99)

(30) Priority Data:

09/156,078

17 September 1998 (17.09.98) US

(71) Applicant: PROCESS CONTROL, INC. [US/US]; Three Christian Centre, 201 West Walnut Street, Wilmington, DE 19801 (US).

(72) Inventors: LAURILA, Melvin, J.; 540 Big Bear Lane, Lexington, KY 40517 (US). BACHMANN, Claus, C.; Silcherst 41, D-75323 Bad Wildbad (DE). KLEIN, Albert, P.; Ahornweg 8, D-72226 Simmersfeld (DE).

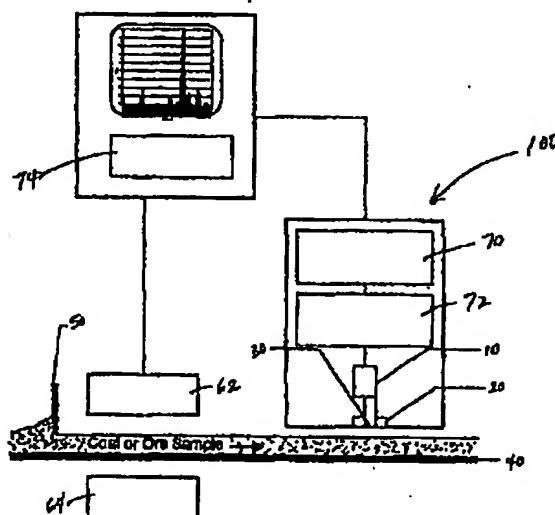
(74) Agents: SCHICKLI, Warren, D. et al.; King and Schickli, Suite 210, 3070 Harrodsburg Road, Lexington, KY 40503 (US).

(81) Designated States: AU, CN, IN, ZA, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

*With international search report.**Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.**
X Übersetzung

(54) Title: X-RAY FLUORESCENCE ELEMENTAL ANALYZER



(57) Abstract

An apparatus for measuring the composition of coal and mineral ores on-line, by bombarding a sample stream with low energy X-rays and measuring the characteristic X-rays fluoresced. The assembly is comprised of one or more X-ray generators (20) mounted in a specific geometry with one or more silicon detectors (10). A representative sample of a flow stream is obtained from a sampling system. Sample presentation to the analyzer is done with a plow (50) or a flow cell to obtain a uniform interrogation zone for the analyzer. Elemental analysis (Aluminum through Silver on the Periodic Table) of the sample is computed from calibration curves generated from a linear relationship with count rates under each peak. Coal ash is determined from a function f (major elements in ash measured, backscattering of incident radiation). Moisture is determined from measuring the attenuation of a microwave beam transmitted through the sample.

BACKGROUND AND SUMMARY OF THE INVENTION

This invention relates to a method and apparatus for analyzing the composition of coal, mineral ores and other products using energy dispersive X-ray fluorescence (XRF) spectroscopy. In the preparation and utilization of coal as a fuel, it is necessary to quantify the chemical and physical characteristics of the coal or ore. Coal purchases or trades are based on one or more of the following physical or chemical characteristics which are measured during the preparation and prior to the use of the coal feedstock:

- Ash content
- Moisture content
- Calorific value content
- Sulfur content
- Elemental analysis

In order to determine these characteristics the coal must be sampled, the sample prepared and then analyzed by standard laboratory procedures as set forth by organizations such as the American Society for Testing and Materials (ASTM) and/or the International Organization of Standardization (ISO). This is a costly and time consuming process requiring anywhere from two hours to more than a day to complete.

To address this problem, a number of coal analyzers have been developed. Most of these are ash analyzers and determine the ash content using dual energy transmission or backscatter of X- or γ - rays generated from two or more radioisotopes. A typical prior art system employs a low energy (<60 KeV) and a high energy (>600 KeV) γ - ray source to measure two signals which can

be correlated to ash and density respectively. Watt (U.S. Patent Nos. 4,090,074 and 4,566,114) uses any number of radioisotope sources from a group consisting of Am-241, Gd-153, Cd-109, Ba-133, Cs-137 and Co-57 to generate a series of incident X- and/or γ - ray energies that are transmitted or scattered through a layer of coal. The determination of the ash or mineral matter content in coal uses a transmission or scatter of X- or γ - rays at an energy where there is a significant difference in the absorption of radiation per unit weight in coal and mineral matter excluding iron (low energy ash measurement), in combination with a measurement of the bulk density (high energy). This is predominately the type of ash analyzer in use.

A variation of this ash analyzer was developed by Page as described in U.S. Patent No. 4,486,894. An iron correction factor was incorporated into the ash determination. Low energy (<60 KeV) radiation bombards a sample with the primary radiation comprising at least two spectrums of energies (46 KeV and 9-17 KeV) to cause radiative reactions in the coal and measuring backscattered radiation in the same energy regions along with a fluoresced iron peak at 6.4 KeV. The fluoresced iron peak can also be related to the sulfur content in certain coals. Page (U.S. Patent No. 4,015,124) approximated the sulfur content of a given type of coal using the multiple linear regression:

$$S = a + bX + cY$$

Where,

S = concentration of sulfur in the coal sample;

X = intensity of fluorescent radiation emitted by the sulfur in the sample;

Y = intensity of fluorescent radiation emitted by the iron in the sample; and

a, b, and c are constants.

However, the sulfur peak (X) could not be accurately measured and the relationship breaks down when iron pyrites (FeS_2) are either not found in sufficient concentrations to detect
5 with a proportional counter or cannot be directly related to the total sulfur content.

Prior art use of X- ray fluorescence for elemental analysis, and particularly, sulfur, has been limited by the fact that the characteristic sulfur $\text{K}\alpha$ X- ray emitted has an energy of only 2.31 KeV. Thus, the X- ray is quickly dissipated in coal (within 1 mm) or even air. To complicate the measurement, sulfur typically occurs in concentrations of less than 0.3% in coal.
10 Marshall, in U.S. Patent No. 4,171,485 states that the use of X- ray fluorescence other than for gaseous materials requires either the preparation or vaporization of a sample in an atmosphere which does not confuse the measurement. In either case, a difficult sampling and sample-preparation problem compounds the errors associated with X- ray fluorescence itself.

The better method in current use for determining sulfur content as well as several other
15 elements present in the coal is to directly measure the different secondary, characteristic γ - ray energies emitted by the different elements when coal or mineral ores are bombarded by neutrons. This measurement process, as described by Marshall (see reference above) and Atwell in U.S. Patent No. 4,582,992 is known in the art as prompt gamma ray neutron activation analysis (PGNAA). This technique is based on the fact that almost all elements when bombarded by slow
20 neutrons capture these neutrons at least momentarily and form a compound nucleus in an excited state. Usually the prompt emission of one or more γ - rays with energies and intensities that are uniquely characteristic of the captured nucleus dissipates most of the excitation energy. Because these prompt γ - rays often have energies in the 2 to 11 MeV range, they can penetrate substantial

quantities of material to reach a γ -ray detector, i.e., NaI(Tl) scintillation detector.

However, because of the high energies necessary to obtain sufficient penetration of flowing coal streams containing particles with top sizes of 2-4 inches, this technique is costly since neutron emitters and the necessary shielding is involved. X-ray fluorescence provides a
5 safer and less expensive alternative if the sample presentation and X-ray detection problems can be solved.

The present invention addresses both sampling and X-ray detection in the design of a system that will mount directly on a sampling system using a thermoelectrically cooled Si-PIN photodiode X-ray detector.

10 Detectors used in X-ray spectroscopy in prior art systems for measuring the composition of coal and mineral ores, have been gas filled proportional counters, typically using a low density fill gas such as Neon or Xenon mixed with Argon. The resolution of 600 eV (FWHM) for proportional counters at low X-ray energies (less than Fe at 6.4 KeV) does not enable accurate determination of elements such as sulfur, silica or aluminum. By contrast, a Si-PIN detector has a
15 resolution of 196 eV (FWHM) for a ^{56}Fe X-ray at 5.9 KeV. Other silicon or semiconductor detectors e.g., Si(Li) can achieve similar high resolutions, but require enclosure in a vacuum cryostat and liquid nitrogen cooling. This seriously limits the applications in which the system can be used. The system must be compact and robust so the detector can be located within 2 inches of the sample surface.

20 As defined herein, an online sampling means refers to a sampling means wherein the sample is nonstationary relative to the analyzer. For example, in one embodiment of the present invention, the analyzer remains in a fixed, stationary position adjacent to a moving sample stream. In another embodiment, the sample remains fixed, and the analyzer is scanned across the

sample.

By mounting the XRF elemental analyzer in close proximity to a moving stream of fine coal or ore, it is possible to obtain direct measurements of characteristic $K\alpha$ and in some cases, $K\beta$, X- rays for many of the elements in the Periodic Table between aluminum and silver. In measuring coal composition, X- ray peaks for aluminum, silica, sulfur, chlorine, potassium, calcium, titanium and iron can be obtained. An ash measurement can also be obtained as a function of the major elements in the ash and/or a backscattered ash peak. A microwave transmitter/receiver assembly is used to relate microwave attenuation or phase shift to moisture content.

Computer control of the sample size and frequency synchronized with the X- ray detection system enables each sample increment to be analyzed and combined so that a statistically valid sample can be obtained in accordance with ASTM and/or ISO sampling practice. As with any sampling device, the XRF elemental analyzer analyzes a portion of a sample stream assumed to be (1) homogeneous and (2) representative of the lot.

15

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a block diagram showing how the XRF Elemental analyzer can be integrated with a mechanical sampling system in a sub-stream configuration.

FIG. 2 is a pictorial view of the analyzer mounted on a sampling system with a layer of coal or ore transported through the analyzer interrogation zone. A plow is used to uniformly shape the surface of the sampled material. The physical layout of the major components including the signal processing elements are shown.

FIG. 2A is an enlarged view of the electronics enclosure and shows a first configuration

of the X- ray generators such that the X- ray source transmission axis and the detection axis are parallel to each other and normal (oriented at 90 degrees) to the sample surface.

FIG. 2B is an enlarged view of the electronics enclosure and shows a second configuration of the X- ray generators such that the X- ray source transmission axis and the
5 detection axis of the detector are oriented generally perpendicular to the sample surface and are aligned to within 30 degrees of each other.

FIG. 3 is a pictorial view of an alternate embodiment where the sample to be analyzed is in slurry form and transported through the interrogation zone in a flow cell. A constant head tank is employed to ensure uniform flow and to minimize air entrainment.

10 FIG. 4 is a typical X- ray fluorescence spectrum from a sample of coal using a ^{55}Fe excitation source. An ^{55}Fe excitation source is equivalent to an X- ray generator with a Cu target.

DETAILED DESCRIPTION OF THE INVENTION

In a preferred embodiment of the present invention, the XRF elemental analyzer 100 is in
15 a sub-stream configuration as shown in FIG. 1, where part of the process stream to be analyzed is diverted by means of a suitable sampling system for presentation to the on-line analyzer 100. If the coal or ore to be analyzed has a top particle size (95% passing) greater than 3/8 inch or 10 mm, then a size reduction stage is necessary to provide a uniform surface to present to the analyzer 100 for interrogation.

20 FIG. 2 illustrates how the XRF elemental analyzer system 100 is configured when mounted on a mechanical sampling means. A coal or ore sample, typically the primary save (after crushing) or the secondary reject, is conveyed 40 past the analyzer 100. A plow 50 is used to shape the layer or bed of material to be interrogated. If a moisture determination is to be made,

a microwave transmitter 64/receiver 62 assembly is mounted above and below the conveyor belt 40 to determine moisture as a function of microwave signal attenuation. The moisture meter also can serve as a sensor to determine the presence of material on the conveyor belt 40. If the microwave signal goes below a threshold limit signaling the presence of material on the conveyor belt 40, the multi-channel analyzer 70 is turned on to acquire counts in as many as 16,000 data channels.

An X- ray tube or generator 20 is employed to bombard the sample with incident radiation in the 3-20 KeV range. Higher energies can be used, but the efficiency of excitation for elements below iron (atomic number 26) in the Periodic Table drops when higher energies are used. An X- ray generator 20 is a pyroelectric crystal that generates energetic electrons which produce X- rays in a target material, i.e., copper or molybdenum. A radioisotope or an X- ray tube can also be used, but is not preferred.

A silicon detector 10 is used to measure the resulting fluorescent radiation. The preferred embodiment uses a thermoelectrically cooled Si-PIN photodiode as an X- ray detector. More than one detector 10 may be used if more than one measuring path is necessary to represent the entire sample. Other types of silicon detectors and cooling systems may be applied.

As defined herein, a backscattering geometry is one in which the source 20 and the detector 10 are disposed generally on the same side of the sample. In contrast, a transmission geometry is one in which the source 20 and the detector 10 are on opposite sides of the sample. In the present invention, a backscattering geometry is preferred for the analysis of solid samples. For liquid samples, a transmission geometry may also be used.

The detector(s) 10 and generator(s) 20 are mounted within 2 inches of the surface of the sample. They are protected by a thin window 30 (0.002-0.01 inches) which maintains a sealed

environment for the electronics. To minimize attenuation of the low energy X- rays by the window 30, low atomic density materials such as polypropylene or polyethylene is used. The film may be coated with a resin or acrylic to increase durability.

The detector 10 and generator 20 are mounted within a 90 degree angle of each other with
5 as small of an angle between them as possible. As defined herein, the transmission axis of the X- ray source 20 is the axis along which X- ray emission reaches a maximum. The detection axis of the X- ray fluorescence detector 20 is defined as the surface normal of the X- ray fluorescence sensing element of the detector 20. In a preferred embodiment, the X- ray source transmission axis and the detection axis of the detector 20 are oriented generally perpendicular to the sample
10 surface and are aligned to within 30 degrees of each other (FIG. 2B). In a particularly preferred embodiment, the X- ray source transmission axis and the detection axis are parallel to each other and normal (oriented at 90 degrees) to the sample surface (FIG. 2A). In a most preferred embodiment, one or more X- ray generators 20 are placed concentrically around a detector 10 and all of the above are perpendicular to the surface of the sample.

15 An alternate configuration in which the detector 10 and generator 20 are mounted on the underside of a chute is also possible.

FIG. 3 depicts another embodiment of the XRF elemental analyzer 200 for slurries. In this case, a sample of the flow stream is obtained from a sample cutter inserted into a pipe. A computer actuated valve 84 controls the flow of the slurry sample to the analyzer 200. Samples
20 from around a processing plant can be sequenced to the analyzer 200 in this manner.

A constant head tank 80 ensures a fixed flow rate through the flow cell 82 containing the X- ray detector(s) 210 and generators(s) 220. It also serves as a de-aerator for slurries containing forth or entrained air.

The flow cell 82 holds the detector 210 and generator 220 in the same configuration as described above. Windows are used to seal the electronics in a water tight chamber. This would include a second X- ray source 220 or a separate density gauge used to measure solids concentration by correlating slurry density (% solids) to attenuation of X- rays or γ - rays. This is done with an incident energy of 20 KeV or higher to minimize the effects of mineralogical composition on the measurement.

In any of the embodiments described, a preamplifier forwards the signal to a shaping amplifier 272 which is connected to the input of a multi-channel analyzer 270 (MCA). The output from the MCA 270 is processed by a computer or programmable logic controller 274 (PLC) to compute the concentrations of various elements in the sample.

FIG. 4 provides an example of the output from the MCA 70, 270 representing an elemental analysis of a western U.S. coal. The areas under each peak correlate to the concentration of each element. These are calibrated using a linear, or sometimes a multiple linear regression (if more than one element occurs together in a certain mineralization) with a laboratory elemental analysis of the sample in accordance with ASTM or ISO procedures. Linear calibration equations are possible to low concentrations of even the lightest elements in the range (e.g. sulfur down to concentrations of 0.5% by weight in ash or 0.05% by weight in coal) because the high peak resolution enables the peak to be distinguished from background and proportionality maintained.

In the case of coal analysis, the ash content can be computed as a function of the major elements in the ash and/or a backscattered peak produced by Compton and Raleigh scattering of the incident beam of radiation. The iron content as measured by the fluoresced Fe K α X- rays is used as a term in the equation to correct for fluctuations in iron which disproportionately affects

the ash computation.

The apparatus described above directly measures the elemental composition of coal and mineral ores using energy dispersive X-ray fluorescence spectroscopy. It provides an accurate ash measurement by improving upon established methods with the use of iron compensation and
5 can resolve a sulfur peak down to 0.5% weight in ash.

We claim:

1. An apparatus for online elemental analysis of a sample comprising
an online sampling means for receiving a sample,
5 at least one X- ray source, and
at least one X- ray fluorescence detector for detecting X- ray fluorescence from said
sample and for producing signals in response to said X- ray fluorescence,
wherein said at least one X- ray source and said at least one X- ray fluorescence detector are
mounted in a geometry that maximizes X- ray detection and sensitivity.
10
2. The apparatus of claim 1 wherein said at least one X- ray fluorescence detector is mounted
within 2 inches of said sample.
3. The apparatus of claim 1 wherein said at least one X- ray source is characterized by a
15 transmission axis and wherein said at least one X- ray fluorescence detector is characterized by a
detection axis, and wherein said transmission axis and said detection axis are aligned to within
30 degrees of the sample surface normal.
4. The apparatus of claim 3 wherein said X- ray transmission axis and said detection axis are
20 parallel to each other and normal to the sample surface.
5. The apparatus of claim 1 wherein said at least one X- ray source and said at least one X- ray
fluorescence detector are disposed in a backscattering geometry.

6. The apparatus of claim 1 further comprising a thin window (0.002-0.010 inches) disposed between the sample and the X-ray detector.

5 7. The apparatus of claim 6 wherein said thin window is comprised of a polymeric core coated with a resin or acrylic.

8. The apparatus of claim 1 wherein further comprising a shaping device for maintaining a uniform sample surface.

10

9. The apparatus of claim 8 wherein said shaping device comprises a plow or a flow cell.

10. The apparatus of claim 8 further comprising a means for controlling said sampling means to provide a uniform sample profile.

15

11. The apparatus of claim 1 further comprising a means for detecting the presence of sufficient sample material.

12. The apparatus of claim 11 wherein said means for detecting the presence of sufficient sample
20 material comprises a microwave, X-ray or γ -ray sensor oriented in a transmission geometry.

13. The apparatus of claim 1 further comprising a microwave moisture reader.

14. The apparatus of claim 1 further comprising a belt scale or density gauge.

15. The apparatus of claim 1 further comprising a flowmeter assembly.

PROCESS STREAM

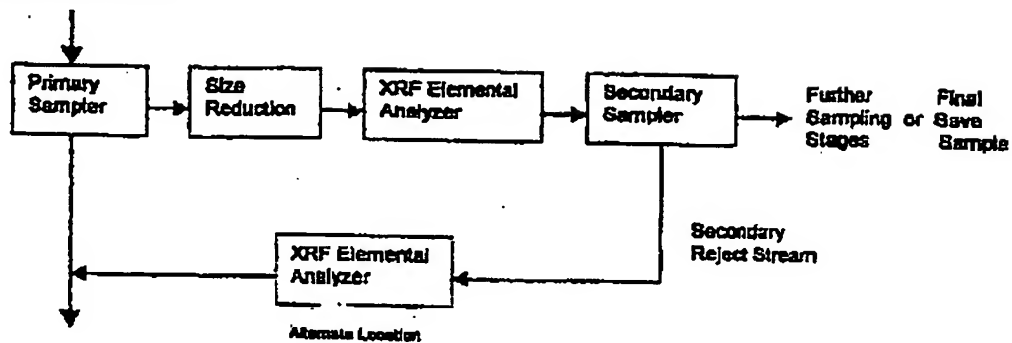


Fig. 1

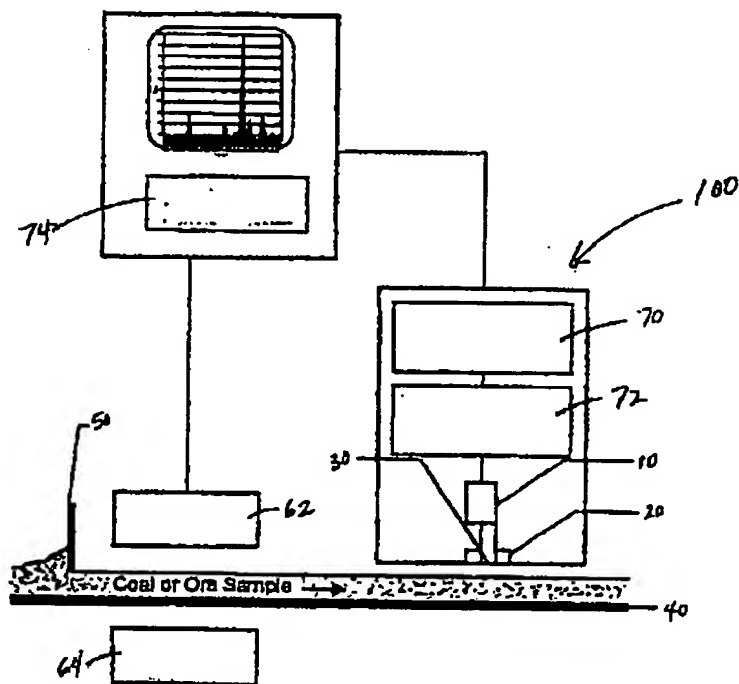


Fig. 2

FIG 2A

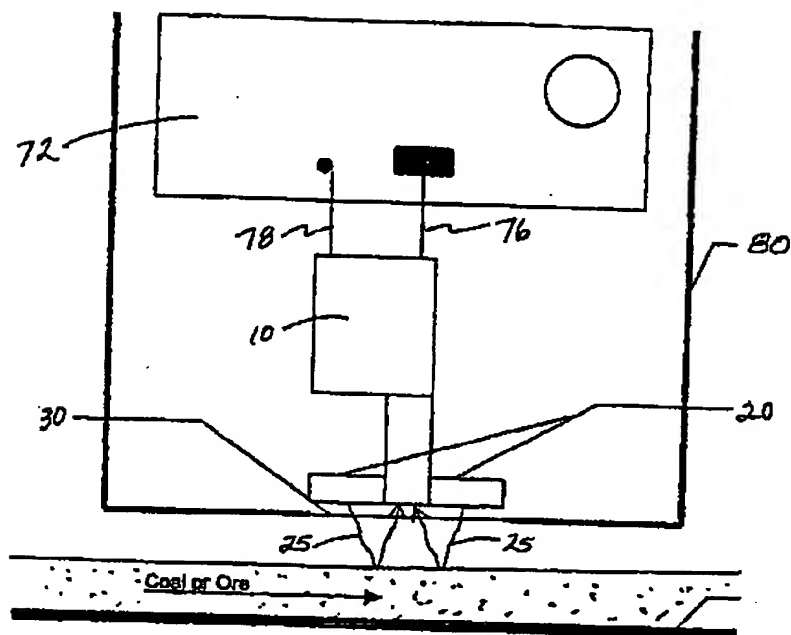
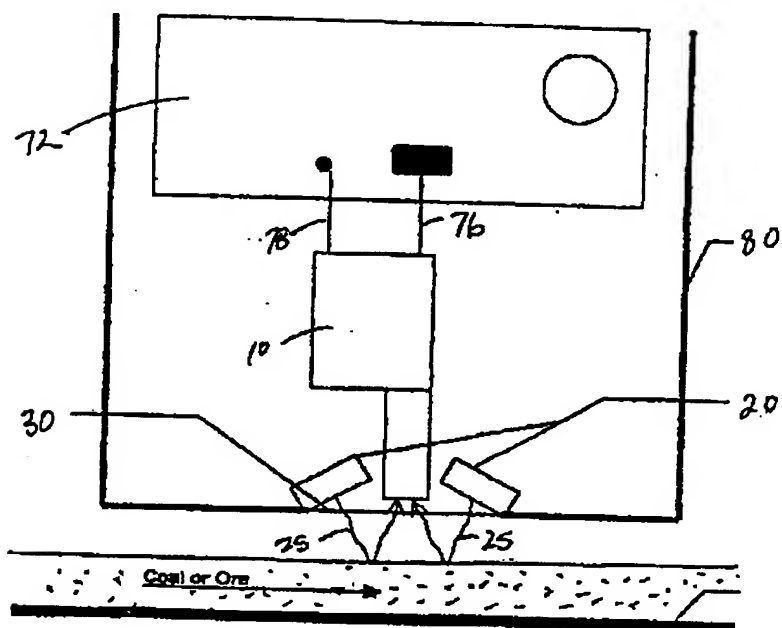


FIG 2B



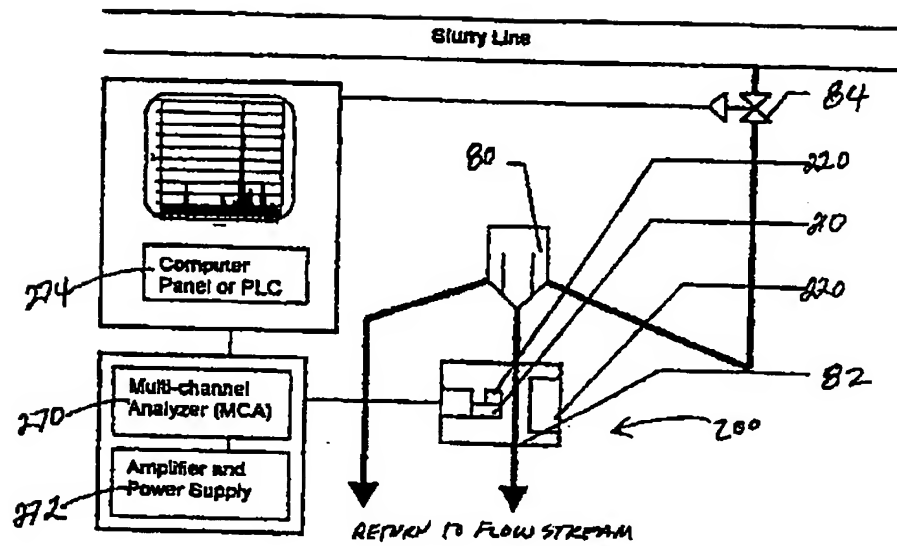


Fig. 3

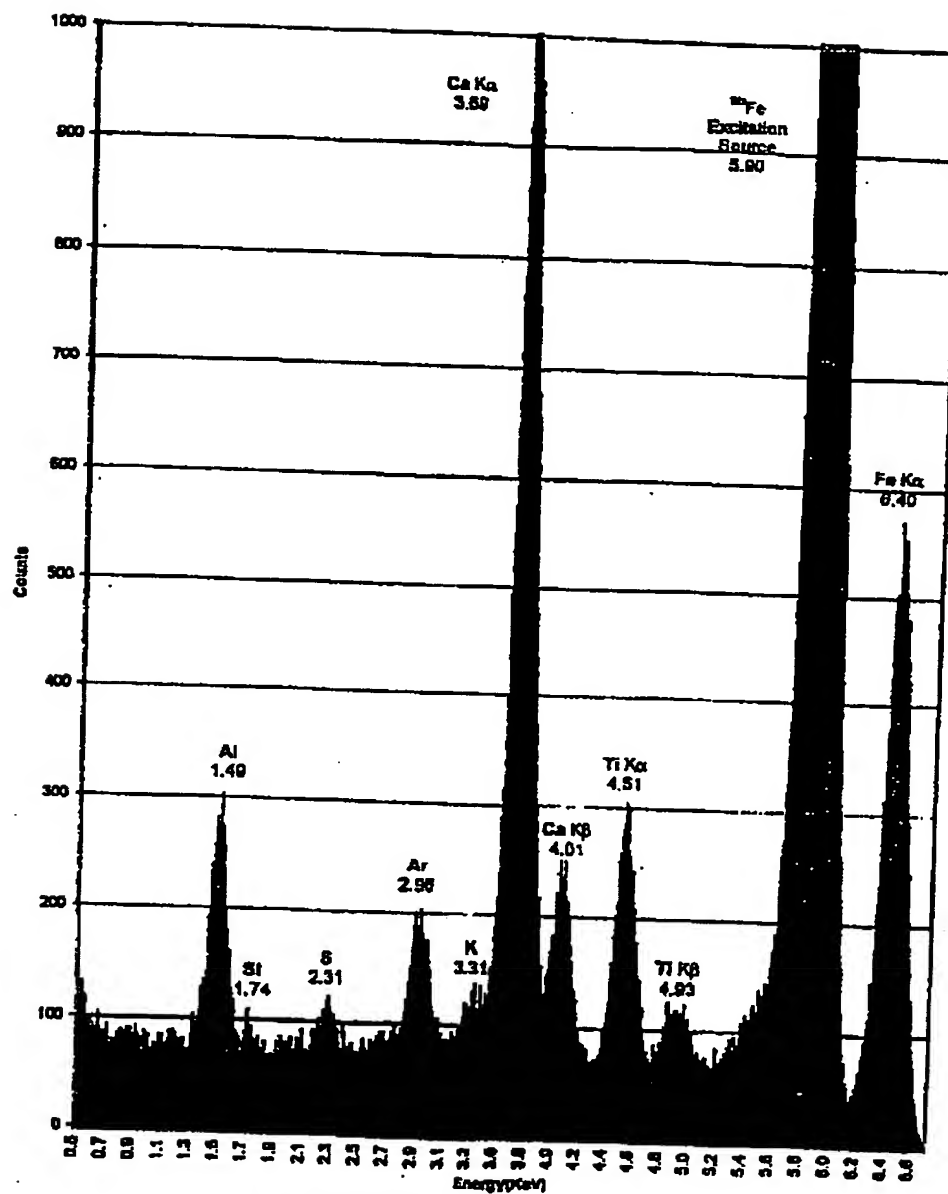


Fig. 4

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☐ BLACK BORDERS

☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

☐ FADED TEXT OR DRAWING

☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING

☐ SKEWED/SLANTED IMAGES

☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS

☐ GRAY SCALE DOCUMENTS

☐ LINES OR MARKS ON ORIGINAL DOCUMENT

☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.